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U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

09/463102

INTERNATIONAL APPLICATION NO.
PCT/US98/15003INTERNATIONAL FILING DATE
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PRIORITY DATE CLAIMED

TITLE OF INVENTION

Fabric Stain Removal Method

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information.

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(I).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application was filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ has been transmitted by the International Bureau.
 - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☒ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

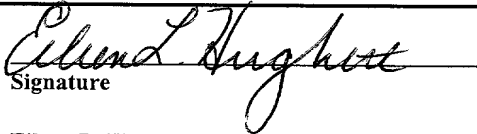
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I hereby certify that this paper/fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to The Assistant Commissioner of Patents, Washington, D.C. 20231

Administrator Mailing Application

Signature

U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/463102		INTERNATIONAL APPLICATION NO. PCT/US98/15003		ATTORNEY'S DOCKET NUMBER 6762	
				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$670	
Surcharge of \$130.00 for furnishing the oath or declaration later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$0	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	17-20 =	0	x \$22.00	\$0	
Independent Claims	2-3 =	0	x \$78.00	\$0	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			\$250.00	\$0	
TOTAL OF ABOVE CALCULATIONS =				\$670	
Processing fee of \$130.00 for furnishing the English translation later than [] 20 [] 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$0	
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Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28,3.31). \$40.00 per property +				\$0	
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B.M. Bolam Patent Division The Procter & Gamble Company Ivorydale Technical Center 5299 Spring Grove Avenue Cincinnati, OH 45217				 Signature <u>Eileen L. Hughett</u> Name <u>34,352</u> Registration Number	

09/463102

FABRIC STAIN REMOVAL METHODTECHNICAL FIELD

5 Fabrics are spot-cleaned with no or minimal visible damage by means of a protective sheet which overlays the stained area during the process.

BACKGROUND OF THE INVENTION

10 Fabrics are often "spot treated" in localized areas to eliminate stains which are judged to be particularly persistent and difficult to remove. Such stain removal processes typically employ various liquids, gel or semi-solid spot remover compositions. In general, the process involves applying the spot remover to the stained area and vigorously rubbing, brushing, or blotting the area until the stain is judged to be satisfactorily removed. The ease-of-removal for any stain can depend on its chemical composition, the amount of the stain and the type of fabric. Cotton, 15 in particular, holds onto stains very tenaciously. Cotton is composed of loosely bound fiber bundles which are extremely porous in nature and prone to swelling and stretching of the weave. Cotton also exhibits a "fuzzy" fabric surface where a multitude of individual fibrils are loosely splayed just above the fabric surface. As the number of loose fibrils is increased, e.g., by mechanical abrasion, so does the 20 level of light scattering across the fabric surface, thereby creating the illusion of excessive garment wear and/or fading.

While occasional, random spot cleaning of garments is not likely to cause much fabric fibrillation, repeated applications in the area of the underarms (to assist malodor removal) or collar/cuff area (to remove body soils) can cause cumulative 25 negative effects. The process of the present invention comprises the overlayment of the stained area with a protective, preferably porous, material during such treatment. The process herein is thus particularly effective for protecting the fabric against abrasion during such spot treatments, especially during multiple cleaning episodes on a particular site. This technique is effective with essentially all garment types, 30 including fine silks, rayon, wool, linen, cotton, polyester, and blends thereof.

BACKGROUND ART

Dry cleaning processes are disclosed in: U.S. 5,547,476 issued 8/20/96 to Siklosi & Roetker; U.S. 5,591,236 issued 1/7/97 to Roetker; U.S. 5,630,847 issued 5/20/97 to Roetker; U.S. 5,630,848 issued 5/20/97 to Young, et al.; U.S. 5,632,780 35 issued 5/27/97 to Siklosi; EP 429,172A1, published 29.05.91, Leigh, et al.; and in U.S. 5,238,587, issued 8/24/93, Smith, et al. Other references relating to dry cleaning compositions and processes, as well as wrinkle treatments for fabrics,

include: GB 1,598,911; and U.S. Patents 4,126,563, 3,949,137, 3,593,544, 3,647,354; 3,432,253 and 1,747,324; and German applications 2,021,561 and 2,460,239, 0,208,989 and 4,007,362. Cleaning/pre-spotting compositions and methods are also disclosed, for example, in U.S. Patents 5,102,573; 5,041,230; 5 4,909,962; 4,115,061; 4,886,615; 4,139,475; 4,849,257; 5,112,358; 4,659,496; 4,806,254; 5,213,624; 4,130,392; and 4,395,261. Sheet substrates for use in a laundry dryer are disclosed in Canadian 1,005,204. U.S. 3,956,556 and 4,007,300 relate to perforated sheets for fabric conditioning in a clothes dryer. U.S. 4,692,277 discloses the use of 1,2-octanediol in liquid cleaners. See also U.S. Patents 10 3,591,510; 3,737,387; 3,764,544; 3,882,038; 3,907,496; 4,097,397; 4,102,824; 4,336,024; 4,606,842; 4,758,641; 4,797,310; 4,802,997; 4,943,392; 4,966,724; 4,983,317; 5,004,557; 5,062,973; 5,080,822; 5,173,200; EP 0 213 500; EP0 261 718; G.B. 1,397,475; WO 91/09104; WO 91/13145; WO 93/25654 and Hunt, D.G. and N.H. Morris, "PnB and DPnB Glycol Ethers", HAPPI, April 1989, pp. 78-82.

15 SUMMARY OF THE INVENTION

The present invention encompasses, in a process for removing stains from a localized area of a fabric, comprising the steps of applying a cleaning composition to said stain and, concurrently or consecutively therewith, applying mechanical action to said stain by means of a cleaning device, the improvement which comprises 20 covering the stain with a sheet of protective covering material which minimizes abrasion of the fabric caused by the mechanical action of the cleaning device. Fibrillation of the fabric, which creates a worn appearance, is thereby minimized.

In a preferred mode, the cleaning composition is a liquid, especially liquids comprising water and surfactant or water, surfactant and organic cleaning solvent. A 25 typical composition comprises water, butoxy propoxy propanol, MgAES surfactant and amine oxide surfactant.

In a highly preferred mode, the mechanical action is provided by the dispenser tip of a bottle which contains multiple portions of the cleaning compositions.

30 A particularly advantageous feature of the present invention is that a more aggressive tip execution for the dispenser bottle can be employed with significant reduction of fabric damage/fibrillation. This is an important point since control of the tip quality during manufacture is sometimes difficult. Some tips may have sharp edges due to processing limitations at the point where the tip is formed in a mold. 35 These sharp edges can increase the risk of fabric damage, and cannot easily be removed without essentially 100% visual inspection via microscopy. The

overlayment technique of this invention minimizes the need for such inspection, thereby making the process more "forgiving" with respect to fabric damage.

A highly preferred process for removing stain from a localized stained area on a fabric thus comprises:

- 5 (a) placing the stained area of the fabric over and in contact with an absorbent material, preferably the fibrous Absorbent Stain Receiver Article or FAM-foam as disclosed hereinafter;
- (b) applying a liquid cleaning composition to said stain from a container having a dispenser spout; and
- 10 (c) concurrently or consecutively with step (b), rubbing or pressing said cleaning composition into said stain using the distal tip of said spout, whereby said stain is transferred into the fluid absorbent material, with the improvement which comprises covering the stain with a sheet of protective covering material which minimizes abrasion of the fabric caused by the mechanical
- 15 action of the spout tip, thereby minimizing fibrillation of the fabric being treated.

The protective covering material used herein in contact with the stained area of the fabric being cleaned can be any woven or non-woven cloth or cloth-like sheet which, itself, has sufficient strength and integrity to withstand the mechanical forces of the stain removal process herein. The tip of the dispenser spout can be concave, convex, or flat. The cleaning composition can be as noted above. In a less preferred mode, the absorbent material can be any conventional material which absorbs the liquid cleaning composition such as cloth, non-woven fabric, disposable paper

20 toweling, and the like.

25 All percentages, ratios and proportions herein are by weight, unless otherwise specified. All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

Protective Covering Material - A wide variety of mesh, porous or non-porous materials can be used as the protective covering material. However, a balance between cleaning effectiveness and fabric protection must be taken into

30 consideration. Of course, an extremely thick layer of the protective covering material would provide 100% protection, but would so interfere with the mechanical action on the stain that stain removal would be minimal. In general, thinner is better than thicker. Fibrous protective materials (e.g., woven or nonwoven cloth) are

35 preferred, but porous or nonporous fabrics or sheet films can also be used. The fiber composition of the protective material can also be varied, though best results are with materials that are reasonably translucent or have sufficient pore size that the

user is able to observe the underlying stain and the progress being made for its removal during the cleaning process.

Of course, the protective material should be sufficiently strong that it can withstand the mechanical force being applied (typically about 400-1000 g force).

- 5 The protective material must be sufficiently supple that it can transmit the force to the underlying fabric/stain. Accordingly, the protective material must be neither so unyielding that the force is not transmitted, nor so compressible that the force is dissipated, or that the tip of the cleaning implement finds itself in a "well" formed in the material.

- 10 It is to be understood that the process herein can be conducted in either of two fashions. In the first, the stain is treated with the cleaning composition, then overlaid with the protective material, followed by application of mechanical force to the protective material which transmits it to the stain. In the second, the stain is overlaid with the protective material, the cleaning composition is applied to the
15 protective material and allowed to pass therethrough, and mechanical force is applied. Of course, in the second option the protective covering material must be porous and permeable to the cleaning composition. The pores in the protective material should preferably not be so large that the tip of the cleaning implement can pass through and come into direct contact with the fabric being treated. In general,
20 for fibrous protective materials the diameter of the fibers should be at least as large as the microscope irregularities on the dispenser tip and should remain so even under in-use compression.

- Moreover, the protective covering material should not be so absorbent with respect to the cleaning composition that it deleteriously competes with the fabric
25 being treated for absorption of the composition.

- Having due regard for the foregoing considerations, convenient, commercially available protective covering materials herein can comprise a wide variety of woven and non-woven fabrics. Non-limiting examples include organza, which is preferred herein. Chiffon can also be used, but cleaning results are
30 somewhat diminished. Physical parameters for these materials are as follows.

	<u>Chiffon</u>	<u>Organza*</u>
Basis Weight (gsm)	49.15	26.33
Caliper at .1 psi (mm)	1.52	1.02
Caliper at 2 psi (mm)	1.27	0.76
5 Opacity (%)	65.5**	54.1**

*Microscopically, the organza has an average of 24 vertical and 25 horizontal polyester threads per quarter inch.

**Higher is more opaque.

Other protective coverings include nylon stocking material, polyvinylidene chloride or polyethylene sheeting such as Glad Wrap™ (a commercial food wrap), polyester fabric, spun-bonded nonwovens, and the like.

The protective material is laid down over the stain. The liquid cleaning solution is applied, preferably from a container with a dispensing spout. The stained area of the garment or fabric swatch is optionally, but preferably, in close contact with any convenient absorbent material as noted above. In a preferred mode, an Absorbent Stain Receiver Article (ASRA; described below) or FAM foam is employed.

Absorbent Material - The absorbent material used herein will be preferably non-linting and capable of absorbing the amount of cleaning composition used to treat the stain. As noted above, various materials can be used for this purpose. The following illustrates two preferred absorbents for use herein, but is not intended to be limiting thereof.

Absorbent Stain Receiver Article ("ASRA") - The ASRA herein can comprise any of a number of absorbent structures which provide a capillary pressure difference through their thickness (Z-direction). When designing the ASRA for use in the spot removal process herein, the following matters are taken into consideration. First, the cleaning solution only removes the soil from the fibers of the fabric even with agitation. If the cleaning solution which carries the soil is allowed to remain in the fabric, the soil will be redeposited on the fabric as the cleaning solution dries. The more complete the removal of cleaning solution from the fabric, the more complete will be the removal of soil.

Second, the fabric being treated is, itself, basically a fibrous absorbent structure which holds liquid (i.e., the cleaning solution) in capillaries between the fibers. While some liquid may be absorbed into the fibers, most of the liquid will be held in interfiber capillaries (this includes capillaries between filaments twisted into a thread). Liquid held in the fabric may be removed by contacting it with another

absorbent structure such as the ASRA, herein. In this process, liquid is transferred from the capillaries of the fabric to the capillaries of the ASRA.

Third, liquid is held in capillaries by capillary pressure. Capillary pressure (P_c) is generally described by the following equation:

5 $P_c = (2\gamma \cos A)/R$ where

γ = the surface tension of the liquid

A = the contact angle between the liquid and the capillary wall

R = the radius of the capillary

Accordingly, capillary pressure is highest in capillaries which have a low contact
10 angle and a small radius. Liquid is held most tightly by high capillary pressure and will move from areas of low capillary pressure to areas of high capillary pressure. Hence, in the subject ASRA which provides a capillary pressure difference through its thickness, liquid will move from low capillary pressure areas to high capillary pressure areas. Capillary pressure can be measured using a variety of techniques,
15 but will employ the liquid cleaning composition as the test liquid.

In reality, most absorbent materials are complex structures comprised of a range of capillary sizes and contact angles. For this discussion, the capillary pressure of a material or capillary pressure zone within a material is defined as the volumetric weighted average of the range of pressures found within that material or
20 zone.

For purposes of illustration, in circumstances wherein a soiled fabric saturated with cleaning solution is in liquid communication contact with two stacked, identical layers of homogeneous absorbent material, such as a paper towel, solution and soil would readily transfer from the fabric to the towel until the
25 capillary pressure is approximately equal in the two materials. At equilibrium a certain amount of solution and soil will remain in the fabric. The exact amount will depend on the basis weight and capillary pressure characteristics of the fabric and towel. A reduced amount of residual solution and soil in the fabric, and therefore better cleaning, would result from replacing the bottom layer (layer not in direct
30 contact with the fabric) of towel with an absorbent layer of capillary pressure higher than that of the towel. By virtue of its higher capillary pressure this absorbent layer will cause more solution to transfer from the low capillary pressure top towel layer to the high capillary pressure absorbent layer which in turn causes more solution to transfer from the fabric to the top towel layer. The result is better cleaning due to
35 less residual solution and soil remaining in the fabric.

This type of multi-layer system is also beneficial when Z-directional pressure is applied to the wetted stained fabric and ASRA. This pressure compresses the

various materials, thereby lowering their void volume and liquid absorption capacity (increasing the % saturation of the materials). This can cause liquid to be squeezed out. The layered structure allows for free liquid to be absorbed by the lower layer, i.e., the one furthest away from the fabric. This lessens the reabsorption of liquid by the fabric. This is especially true if the bottom layer (layer of highest capillary pressure) is also relatively incompressible (retains a higher percentage of its void volume under pressure) compared to the top layer (layer of lower capillary pressure). In this case it may be desirable for the top layer to be resiliently compressible so as to express liquid under pressure which can be absorbed by the bottom layer.

Thus the ASRA can comprise two or more relatively distinct layers which differ in capillary pressure. As can be seen from the capillary pressure equation, a difference in capillary pressure can be achieved by varying the capillary size or the contact angle between the cleaning solution and the ASRA. Both factors can be controlled by the composition of the ASRA. The contact angle portion of the equation can also be affected by chemical treatment of the ASRA with, for example, a surfactant to lower the contact angle or a water repellent material such as silicone to increase contact angle.

The effectiveness of an ASRA comprising multiple layers of differing capillary pressure can be enhanced by locating most of the total absorbent capacity in the high capillary pressure portion. The top fabric facing layer need only be thick enough to insulate the fabric from the liquid held in the bottom layer.

The effectiveness of the layered ASRA can be further enhanced by selecting the low capillary pressure portion to have a capillary pressure higher than that of the fabric being treated.

In an ASRA comprised of two or more layers differing in capillary pressure, the pattern of capillary pressure change can be characterized as "stepped". Through the thickness of the ASRA there is a sharp change or step in capillary pressure at the layer interfaces. It will be appreciated that the ASRA herein need not comprise multiple distinct layers, but rather can comprise a single layer structure with a relatively continuous capillary size gradient through its thickness.

Fibers - The ASRA can be made from a variety of materials including fibrous absorbents and foams. Useful fibrous absorbents include nonwoven fabrics (carded, hydroentangled, thermal bonded, latex bonded, meltblown, spun, etc.), thermal bonded airlaid nonwovens ("TBAL"), latex bonded airlaid nonwovens ("LBAL"), multi-bonded airlaid nonwovens ("MBAL" combined latex and thermal bonded), wet laid paper, woven fabrics, knitted fabrics or combination of materials (i.e., top layer of a carded nonwoven, and a bottom layer of wet laid paper). These

fibrous absorbents can be manufactured using a wide variety of fibers including both natural and synthetic fibers. Useful fibers include wood pulp, rayon, cotton, cotton linters, polyester, polyethylene, polypropylene, acrylic, nylon, multi-component binder fibers, etc. Multiple fiber types can be blended together to make useful materials. Useful foam materials include polyurethane foams and high internal phase emulsion foams. The critical factor is to have a difference in capillary pressure within the thickness of the ASRA. A broad range of fiber sizes can be employed. A typical, but non-limiting range of diameters is from about 0.5 micrometers to about 60 micrometers. For meltblown, the preferred fibers are less than about 10 micrometers. Typical spun-bond and synthetic staple fibers range in diameter from about 14 to about 60 micrometers. In general, one selects smaller diameter fibers for the high capillary pressure layer and higher diameters for low capillary pressure. Fiber length can depend on the forming process that is being used and the desired capillary pressure. Spun-bonds comprise a substantially continuous fiber. For air-laid fibers, 4-6 mm is typical. For carded fibers the range is typically 25-100 mm. In addition, it has now been found that enriching the upper layer in bicomponent fibers decreases linting during use. Cleaning can also be enhanced by making the top layer rich in synthetic (e.g., bicomponent) fibers due to their lipophilic nature which aids in the removal of oily stains from the fabric being treated.

Absorbent gelling materials ("AGM") such as those sometimes referred to in the diaper art as 'supersorbers' can be added to either or both layers of the receiver or as a discrete layer between the fiber layers or on the back of the bottom layer of the ASRA. Functionally, the AGM provides additional liquid absorption capacity and serves to drain the capillaries in the ASRA structure which helps to maintain the capillary pressure gradient as liquid is absorbed.

In light of the foregoing considerations, the ASRA herein can be defined as an absorbent structure which has a capillary pressure difference through its thickness (Z-direction). In a typical, but non-limiting mode, this can be achieved by having relatively larger capillaries (for example 50-100 micrometers radius) in the upper, liquid-receiving portion of the ASRA which is placed in contact with the fabric being treated. The lower, liquid-storage portion having relatively smaller capillaries (for example 5-30 micrometers radius). Irrespective of the size employed, it is desirable that the difference in average capillary pressure between the two layers be large enough that the overlap in capillary pressure range between the two layers is minimized.

Basis Weight - The basis weight of the ASRA can vary depending on the amount of cleaning solution which must be absorbed. A preferred 127 mm X 127 mm receiver absorbs about 10-50 grams of water. Since very little liquid is used in the typical stain removal process, much less capacity is actually required. A typical TBAL ASRA pad weighs about 4-6 grams. A useful range is therefore about 1 gram to about 7 grams. A variety of sizes can be used, e.g., 90 mm x 140 mm.

Size - The preferred size of the ASRA is about 127 mm X 127 mm, but other sizes can be used, e.g., 90 mm x 140 mm. The shape can also be varied.

Thickness - The overall thickness of the preferred ASRA is about 3 mm (120 mils) but can be varied widely. The low end may be limited by the desire to provide absorbency impression. A reasonable range is 25 mils to 200 mils.

Lint Control Binder Spray - The ASRA is preferably dust free. Some materials are naturally dust free (synthetic nonwoven fabrics). Some, generally cellulose containing materials, can be dusty because not all the fibers are bonded. Dust can be reduced by bonding substantially all the fibers which reside on or near the surface of the ASRA which contacts the fabric being treated. This can be accomplished by applying resins such as latex, starch, polyvinyl alcohol or the like. Cold or hot crimping, sonic bonding, heat bonding and/or stitching may also be used along all edges of the receiver to further reduce linting tendency.

Backing Sheet - The ASRA is generally sufficiently robust that it can be used as-is. However, in order to prevent strike-through of the liquid onto the table top or other treatment surface selected by the user, it is preferred to affix a liquid-impermeable barrier sheet to the bottom-most surface of the lower layer. This backing sheet also improves the integrity of the overall article. The bottom-most layer can be extrusion coated with an 0.5-2.0 mil, preferably 1.0 mil, layer of polyethylene or polypropylene film using conventional procedures. A film layer could also be adhesively or thermally laminated to the bottom layer. The film layer is designed to be a pinhole-free barrier to prevent any undesired leakage of the cleaning composition beyond the receiver. This backing sheet can be printed with usage instruction, embossed and/or decorated, according to the desires of the formulator. The ASRA is intended for use outside the dryer. However, since the receiver may inadvertently be placed in the dryer and subjected to high temperatures, it is preferred that the backing sheet be made of a heat resistant film such as polypropylene or nylon.

Colors - White is the preferred color for the ASRA as it allows the user to observe transfer of the stain from the fabric to the receiver. However, there is no

functional limit to the choice of color. The backing sheet can optionally be a contrasting color.

Embossing - The ASRA can also be embossed with any desired pattern or logo.

- 5 Manufacture - A typical, but non-limiting, embodiment of the ASRA herein is a TBAL material which consists of an upper, low capillary pressure layer which is placed in liquid communication contact with the fabric being treated and a bottom high capillary pressure layer. The ASRA can be conveniently manufactured using procedures known in the art for manufacturing TBAL materials; see U.S. 4,640,810.
- 10 As an overall proposition, TBAL manufacturing processes typically comprise laying-down a web of absorbent fibers, such as relatively short (2-4 mm) wood pulp fibers, in which are commingled relatively long (4-6 mm) bi-component fibers. The sheath of the bicomponent fiber melts with the application of heat to achieve thermal bonding. The bi-component fibers intermingled throughout the wood pulp fibers
- 15 thereby act to 'glue' the entire mat together. Both layers in one embodiment of the ASRA herein can be a homogeneous blend of wood pulp fibers and bi-component thermal bonding fibers. In a more preferred embodiment, the top layer is 100% concentric bi-component fiber comprising 50:50 (wt.) polyethylene (PE) and polypropylene (PP) comprising a PP core enrobed in an outer sheath of PE. The
- 20 gradient is achieved by providing a higher proportion of bicomponent bonding fibers in the top layer compared to the bottom layer. Using a TBAL process as described in U.S. 4,640,810, the top, low capillary pressure layer is formed by a first forming station from 100% bicomponent fiber (AL-Thermal-C, 1.7 dtex, 6 mm long available from Danaklon a/s). Basis weight of this all-bicomponent top layer is
- 25 approximately 30 gsm (grams/meter²). The bottom, high capillary pressure layer is formed upon the top layer by second and third forming stations from a fiber blend consisting of approximately 72% wood pulp (Flint River Fluff available from Weyerhaeuser Co.) and approximately 28% bi-component binder fiber. Basis weight of this bottom layer is approximately 270 gsm. Each of the second and third
- 30 forming station deposits approximately half of the total weight of the bottom layer. The two layers are then calendered to provide a final combined thickness of approximately 3 mm. Subsequently, a 1.0 mil coating of polypropylene is extrusion coated onto the exposed surface of the bottom layer. Individual receivers are cut to 127 mm X 127 mm size. In one optional mode, since the material will be wound
- 35 into a roll before applying the back sheet, a binder (e.g., latex - Airflex 124 available from Air Products) can be applied to the exposed surface of the lower layer prior to thermal bonding to prevent transfer of dust to the top all-bicomponent layer.

Alternatively, a non-linting sheet can be placed on the ASRA during roll-up to prevent linting due to contact between the surfaces.

The composition and basis weights of the layers can be varied while still providing an ASRA with the desired capillary pressure gradient and cleaning performance. Non-limiting examples are as follows.

	Bottom High Capillarity Layer Composition		Top Low Capillarity	
	Ratio Pulp/Bicomponent Fiber Basis Weight		100% Bicomponent Basis Weight	
	<u>270 gsm (wt./wt.)</u>		<u>(gsm)</u>	
	72/28		20	
10	72/28		10	
	79/21		30	
	79/21		20	
	79/21		10	
	86/14		10	
15	86/14		20	
	86/14		30	

Another TBAL structure useful herein comprises a top (fluid receiving) layer comprising about 50% bicomponent fiber and 50% wood pulp, with a basis weight of about 50 gsm. The bottom layer is an 80/20 (wt.) blend of wood pulp and bicomponent staple fiber with a basis weight of about 150 gsm.

It will be appreciated by those skilled in the art of absorbent materials that the foregoing ASRA's will provide layers or zones of relatively higher and lower capillarity. The terms "high" and "low"/"higher" and "lower" are to be understood as being relative to the capillarities of the layers or zones in ASRA's herein and not to some external standard. Accordingly, as long as the capillarity of the upper, fluid receiving layer or zone is lower than that of the underlying layer or zone, the ASRA's will function in their intended manner. However, for comparison purposes and not by way of limitation, the capillarity of the "low" capillarity layer will typically be in the range from about 2 cm of water to about 15 cm of water, and the capillarity of the "high" capillarity layer will typically be in the range from about 10 cm of water to about 50 cm of water. (Capillarity can be measured using the cleaning composition of interest according to the procedure reported at Column 11, U.S. Patent 4,610,678, Weisman, et al., issued September 6, 1986, with reference to the basic procedure and apparatus design as reported by Burgeni and Kapur, "Capillary Sorption Equilibria in Fiber Masses", *Textile Research Journal*, 37 (1967) 362, which publications are incorporated herein by reference.)

Usage Conditions - The ASRA herein is intended to be made so inexpensively that it can be discarded after a single use. However, the structures are sufficiently robust that multiple re-uses are possible. In any event, the user should preferably position the article such that "clean" areas are positioned under the stained areas of the fabric being treated in order to avoid release of old stains from the ASRA back onto the fabric.

Another type of absorbent useful herein comprises Functional Absorbent Materials ("FAM's") which are in the form of water-absorbent foams having a controlled capillary size. The physical structure and resulting high capillarity of FAM-type foams provide very effective water absorption, while at the same time the chemical composition of the FAM typically renders it highly lipophilic. Thus, the FAM can essentially provide both hydrophilicity and lipophilicity simultaneously. (FAM foams can be treated to render them hydrophilic. Both the hydrophobic or hydrophilic FAM can be used herein.)

The acquisition and absorbency of the FAM with respect to the liquid cleaning compositions herein is superior to most other types of absorbent materials. For example, the FAM has a capacity of about 6 g (H₂O) per gram of foam at a suction pressure of 100 cm of water. By contrast, cellulose wood fiber structures have substantially no capacity above about 80 cm of water. Since, in the present process the volume of liquid cleaning composition used is relatively low (a few milliliters is typical) the amount of FAM used can be small. This means that the pad of FAM which underlays the stained area of fabric can be quite thin and still be effective.

The manufacture of FAM-type foams for use as the ASRA herein forms no part of the present invention. The manufacture of FAM foam is very extensively described in the patent literature; see, for example: U.S. 5,260,345 to DesMarais, Stone, Thompson, Young, LaVon and Dyer, issued November 9, 1993; U.S. 5,268,224 to DesMarais, Stone, Thompson, Young, LaVon and Dyer, issued December 7, 1993; U.S. 5,147,345 to Young, LaVon and Taylor, issued September 15, 1992 and companion patent U.S. 5,318,554 issued June 7, 1994; U.S. 5,149,720 to DesMarais, Dick and Shiveley, issued September 22, 1992 and companion patents U.S. 5,198,472, issued March 30, 1993 and U.S. 5,250,576 issued October 5, 1993; U.S. 5,352,711 to DesMarais, issued October 4, 1994; PCT application 93/04115 published March 4, 1993, and U.S. 5,292,777 to DesMarais and Stone, issued March 8, 1994; U.S. 5,387,207 to Dyer, DesMarais, LaVon, Stone, Taylor and Young, issued February 7, 1995; U.S. 5,500,451 to Goldman and Scheibel, issued March 19,

1996; and U.S. 5,550,167 to DesMarais, issued August 27, 1996, all incorporated herein by reference.

Absorbents made of FAM foam can be used in either of two ways. In one mode, the uncompressed foam is used. Uncompressed FAM pads having a thickness in the range of about 0.3 mm to about 15 mm are useful. In another mode, the FAM foam can be used in a compressed state which swells as liquid cleaner with its load of stain material is imbibed. Compressed FAM foams having thicknesses in the range of about 0.02 inches (0.5 mm) to about 0.185 inches (4.7 mm) are suitable herein.

The preparation of FAM foam (also sometimes referred to in the literature as "HIPE", i.e., high internal phase emulsion) is described in the patents cited hereinabove. The following Example illustrates the preparation of a compressed foam for use herein.

Preparation of Emulsion and FAM Foams Therefrom

A) Emulsion Preparation

Anhydrous calcium chloride (36.32 kg) and potassium persulfate (189 g) are dissolved in 378 liters of water. This provides the water phase stream to be used in a continuous process for forming the emulsion.

To a monomer combination comprising distilled divinylbenzene (42.4% divinylbenzene and 57.6% ethyl styrene) (1980 g), 2-ethylhexyl acrylate (3300 g), and hexanedioldiacrylate (720 g) is added a diglycerol monooleate emulsifier (360 g), ditallow dimethyl ammonium methyl sulfate (60g), and Tinuvin 765 (15g). The diglycerol monooleate emulsifier (Grindsted Products; Brabrand, Denmark) comprises approximately 81% diglycerol monooleate, 1% other diglycerol monoesters, 3% polyols, and 15% other polyglycerol esters, imparts a minimum oil/water interfacial tension value of approximately 2.7 dyne/cm and has an oil/water critical aggregation concentration of approximately 2.8 wt. %. After mixing, this combination of materials is allowed to settle overnight. No visible residue is formed and all of the mixture is withdrawn and used as the oil phase in a continuous process for forming the emulsion.

Separate streams of the oil phase (25°C) and water phase (53°-55°C) are fed to a dynamic mixing apparatus. Thorough mixing of the combined streams in the dynamic mixing apparatus is achieved by means of a pin impeller. The pin impeller comprises a cylindrical shaft of about 36.8 cm in length with a diameter of about 2.5 cm. The shaft holds 6 rows of pins, 3 rows having 33 pins and 3 rows having 32 pins, each having a diameter of 0.5 cm extending outwardly from the central axis of the shaft to a length of 2.5 cm. The pin impeller is mounted in a cylindrical sleeve

which forms the dynamic mixing apparatus, and the pins have a clearance of 1.5 mm from the walls of the cylindrical sleeve.

A minor portion of the effluent exiting the dynamic mixing apparatus is withdrawn and enters a recirculation zone; see PCT U.S. 96/00082 published 18 July 96 and EPO 96/905110.1 filed 11 January 96. The Waukesha pump in the recirculation zone returns the minor portion to the entry point of the oil and water phase flow streams to the dynamic mixing zone.

The combined mixing and recirculation apparatus set-up is filled with oil phase and water phase at a ratio of 4 parts water to 1 part oil. The dynamic mixing apparatus is vented to allow air to escape while filling the apparatus completely. The flow rates during filling are 7.6 g/sec oil phase and 30.3 cc/sec water phase.

Once the apparatus set-up is filled the vent is closed. Agitation is then begun in the dynamic mixer, with the impeller turning at 1450 RPM and recirculation is begun at a rate of about 30 cc/sec. The flow rate of the water phase is then steadily increased to a rate of 151 cc/sec over a time period of about 1 min., and the oil phase flow rate is reduced to 3 g/sec over a time period of about 3 min. The recirculation rate is steadily increased to about 150 cc/sec during the latter time period. The back pressure created by the dynamic mixer and static mixing zone (TAH Industries Model Number 101-212) at this point is about 14.7 PSI (101.4 kPa), which represents the total back pressure of the system. The Waukesha pump speed is then steadily decreased to a yield a recirculation rate of about 75 cc/sec. The impeller speed is then steadily increased to 1550 RPM over a period of about 10 seconds. The back pressure increases to about 16.3 PSI (112 kPa).

B) Polymerization of Emulsion

The emulsion flowing from the static mixer is collected in a round polypropylene tub, 17 in. (43 cm) in diameter and 7.5 in (10 cm) high, with a concentric insert made of Celcon plastic. The insert is 5 in (12.7 cm) in diameter at its base and 4.75 in (12 cm) in diameter at its top and is 6.75 in (17.1 cm) high. The emulsion-containing tubs are kept in a room maintained at 65 °C. for 18 hours to bring about polymerization and form the foam.

C) Foam Washing and Dewatering

The cured FAM foam is removed from the curing tubs. The foam at this point has residual water phase (containing dissolved emulsifiers, electrolyte, initiator residues, and initiator) about 45-55 times (45-55X) the weight of polymerized monomers. The foam is sliced with a sharp reciprocating saw blade into sheets which are 0.185 inches (0.47 cm) in thickness. These sheets are then subjected to compression in a series of 2 porous nip rolls equipped with vacuum which gradually

reduce the residual water phase content of the foam to about 6 times (6X) the weight of the polymerized material. At this point, the sheets are then resaturated with a 1.5% CaCl_2 solution at 60°C ., are squeezed in a series of 3 porous nip rolls equipped with vacuum to a water phase content of about 4X. The CaCl_2 content of the foam is between 8 and 10 %.

The foam remains compressed after the final nip at a thickness of about 0.025 in. (0.063 cm). The foam is then dried in air for about 16 hours. Such drying reduces the moisture content to about 9-17 % by weight of polymerized material. At this point, the foam sheets are very drapeable. In this collapsed state, the density of the foam is about 0.14 g/cc. A fluid-impermeable backing sheet (e.g., 1 mil polypropylene) can optionally be applied. If desired, the FAM sheet can be encased in a liquid permeable fabric (e.g., nylon stocking material or woven or non-woven fabric such as spunbonded polyester; Reemay; basis weight about 18 gsm) to reinforce the FAM against flaking, in-use.

As noted above, for use as a stain receiver in the localized stain cleaning operation herein, a sheet of the ASRA or the FAM is placed beneath and in close contact with the backside of the stained area of a fabric. The cleaning composition is mechanically manipulated into the stain, and, together with its load of stain material, is transferred through the fabric and into the underlying ASRA or FAM pad.

Compositions - The user of the present process can be provided with various, preferably liquid, compositions to use as spot cleaning compositions. One problem associated with known fabric cleaning compositions is their tendency to leave visible residues on fabric surfaces. Such residues are problematic and are preferably to be avoided herein since the present process does not involve conventional immersion or rinse steps. Accordingly, the compositions herein should, most preferably, be substantially free of various polyacrylate-based emulsifiers, polymeric anti-static agents, inorganic builder salts and other residue-forming materials, except at low levels of about 0.1%-0.3%, and preferably 0%, of the final compositions. Stated otherwise the compositions herein should be formulated so as to leave substantially no visible residue on fabrics being treated according to the practice of this invention.

Accordingly, in a preferred aspect of this invention there are provided liquid cleaning (i.e., spot-cleaning) compositions which are substantially free of materials which leave visible residues on the treated fabrics. This necessarily means that the preferred compositions are formulated to contain the highest level of volatile materials possible, preferably water, typically about 95%, preferably about 97.7%, a cleaning solvent such as BPP at a low, but effective, level, typically about 1% to

about 4%, preferably about 2%, and surfactant at levels of about 0.1 to about 0.7%. Advantageously, when thus formulated such compositions exist as aqueous solutions rather than as suspensions or emulsions. Thus, such compositions do not require use of additional emulsifiers, thickening agents, suspending agents, and the like, all of which can contribute to the formation of undesirable visible residues on the fabric.

Indeed, as an overall proposition, any of the chemical compositions which are used to provide the spot removal function herein comprise ingredients which are safe and effective for their intended use, and, as noted above, preferably do not leave unacceptable amounts of visible residues on the fabrics. While conventional laundry detergents are typically formulated to provide good cleaning on cotton and cotton/polyester blend fabrics, the compositions herein must be formulated to also safely and effectively clean and refresh fabrics such as wool, silk, rayon, rayon acetate, and the like. In addition, the compositions herein comprise ingredients which are specially selected and formulated to minimize dye removal or migration from the stain site of fugitive, unfixed dye from the fabrics being cleaned. In this regard, it is recognized that the solvents typically used in immersion dry cleaning processes can remove some portion of certain types of dyes from certain types of fabrics. However, such removal is tolerable in immersion processes since the dye is removed relatively uniformly across the surface of the fabric. In contrast, it has now been determined that high concentrations of certain types of cleaning ingredients at specific sites on fabric surfaces can result in unacceptable localized dye removal. The preferred compositions herein are formulated to minimize or avoid this problem.

The dye removal attributes of the present compositions can be compared with art-disclosed cleaners using photographic or photometric measurements, or by means of a simple, but effective, visual grading test. Numerical score units can be assigned to assist in visual grading and to allow for statistical treatment of the data, if desired. Thus, in one such test, a colored garment (typically, silk, which tends to be more susceptible to dye loss than most woolen or rayon fabrics) is treated by padding-on cleaner/refreshers using an absorbent, white paper hand towel. Hand pressure is applied, and the amount of dye which is transferred onto the white towel is assessed visually. Numerical units ranging from: (1) "I think I see a little dye on the towel"; (2) "I know I see some dye on the towel"; (3) "I see a lot of dye on the towel"; through (4) "I know I see quite a lot of dye on the towel" are assigned by panelists.

In addition to the foregoing considerations, the compositions used herein are preferably formulated such that they are easily dispensed and not so adhesive in nature that they render dispensing from the container to be unhandy or difficult. However, and while not intending to be limiting of the present invention, the

preferred compositions disclosed herein afford a spot-cleaning process which is both effective and aesthetically pleasing when used in the manner disclosed herein.

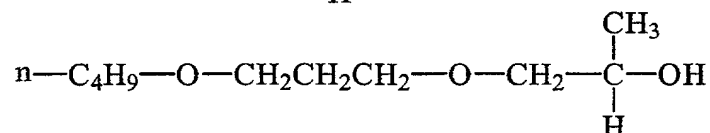
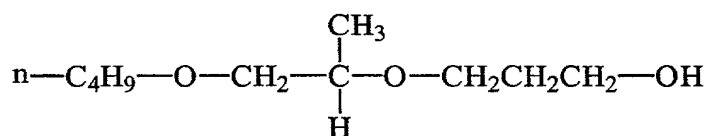
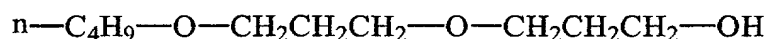
Aqueous Stain Cleaning Compositions

- 5 (a) Water -The preferred, low residue compositions herein may comprise from about 90%, preferably from about 95.5% to about 99.9%, by weight, of water.
- 10 (b) Solvent - The compositions herein may comprise from about 0% to about 10%, by weight, of butoxy propoxy propanol (BPP) solvent or other solvents as disclosed herein. Preferred spot cleaners will comprise 1-4% BPP.
- 15 (c) Surfactant - The compositions herein may optionally comprise from about 0.05% to about 2%, by weight, of surfactants, such as MgAES and NH₄AES, amine oxides, ethoxylated alcohols or alkyl phenols, alkyl sulfates, and mixtures thereof. The use of surfactants limited to the lower end of the range is preferred for some dyes and fabric types. Typically, the weight ratio of BPP solvent:surfactant(s) is in the range of from about 10:1 to about 1:1. One preferred composition comprises 2% BPP/0.25% Neodol 23 6.5. Another preferred composition comprises 4% BPP/0.4% AS. Most preferred is a composition of 2% BBP/0.3% MgAE₁S/0.03% dodecyl dimethyl amine oxide.
- 20 (d) Optionals - The compositions herein may comprise minor amounts of various optional ingredients, including bleach stabilizers, perfumes, preservatives, and the like. If used, such optional ingredients will typically comprise from about 0.05% to about 2%, by weight, of the compositions, having due regard for residues on the cleaned fabrics.
- 25 (e) Bleach - The compositions herein may also optionally comprise from about 0.25% to about 7%, by weight, of hydrogen peroxide. Preferred spot cleaners will comprise 0.5 to about 3% hydrogen peroxide. It will be appreciated that peroxide sources other than H₂O₂ can be used herein. Thus, various per-acids, per-salts, per-bleaches and the like
- 30 known from the detergency art can be used. However, such materials are expensive, difficult to formulate in liquid products, can leave residues on fabrics and offer no special advantages over H₂O₂ when used in the present manner.
- 35 (f) Chelator -Compositions which contain H₂O₂ will also typically contain a chelating agent. The chelating agent is selected from those which, themselves, are stable in aqueous H₂O₂ and which stabilize the H₂O₂ by chelating vagrant metal ions. Such chelating agents are

typically already present at low, peroxide-stabilizing amounts (0.01-1%) in commercial sources of hydrogen peroxide. A variety of phosphonate chelators are known in stabilizing H₂O₂. The amino phosphonates are especially useful for this purpose. Various amino phosphonates are available as under the DEQUEST® trade name from the Monsanto Company, St. Louis, Missouri. Representative, but non-limiting, examples include ethylenediamine tetrakis (methylene phosphonic) acid, diethylenetriamine penta(methylene phosphonic) acid, and the water-soluble salts thereof. Amino tris(methylene phosphonic) acid or its water-soluble salts (as DEQUEST 2000®) is a preferred chelator.

The pH range of the cleaning compositions helps provide stability to the hydrogen peroxide and is typically in the acid-slightly basic range from about 3 to about 8, preferably about 6.

Organic Solvent - The preferred cleaning solvent herein is butoxy propoxy propanol (BPP) which is available in commercial quantities as a mixture of isomers in about equal amounts. The isomers, and mixtures thereof, are useful herein. The isomer structures are as follows:



While the cleaning compositions herein function quite well with only the BPP, water and surfactant, they may also optionally contain other ingredients to further enhance their stability. Hydrotropes such as sodium toluene sulfonate and sodium cumene sulfonate, short-chain alcohols such as ethanol and isopropanol, and the like, can be present in the compositions. If used, such ingredients will typically comprise from about 0.05% to about 5%, by weight, of the stabilized compositions herein.

Surfactants - Nonionics such as the ethoxylated C₁₀-C₁₆ alcohols, e.g., NEODOL 23-6.5, can be used in the compositions. The alkyl sulfate surfactants which may be used herein as cleaners and to stabilize aqueous compositions are the C₈-C₁₈ primary ("AS"; preferred C₁₀-C₁₄, sodium salts), as well as branched-chain

and random C₁₀-C₂₀ alkyl sulfates, and C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula CH₃(CH₂)_x(CHOSO₃⁻M⁺) CH₃ and CH₃ (CH₂)_y(CHOSO₃⁻M⁺) CH₂CH₃ where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, as well as unsaturated sulfates such as oleyl sulfate. Alkyl ethoxy sulfate (AES) surfactants used herein are conventionally depicted as having the formula R(EO)_xSO₃Z, wherein R is C₁₀-C₁₆ alkyl, EO is -CH₂CH₂-O-, x is 1-10 and can include mixtures which are conventionally reported as averages, e.g., (EO)_{2.5}, (EO)_{6.5} and the like, and Z is a cation such as sodium ammonium or magnesium (MgAES). The C₁₂-C₁₆ alkyl dimethyl amine oxide surfactants can also be used. A preferred mixture comprises MgAE₁S/C₁₂ dimethyl amine oxide at a weight ratio of about 10:1. Other surfactants which improve phase stability and which optionally can be used herein include the polyhydroxy fatty acid amides, e.g., C₁₂-C₁₄ N-methyl glucamide. AS stabilized compositions preferably comprise 0.1%-0.5%, by weight, of the compositions herein. MgAES and amine oxides, if used, can comprise 0.01%-2%, by weight, of the compositions. The other surfactants can be used at similar levels.

Other Optionals - In addition to the water, the preferred BPP solvent, the optional H₂O₂ and the surfactants disclosed above, liquid compositions used herein may comprise various optional ingredients, such as perfumes, preservatives, brighteners, salts for viscosity control, pH adjusters or buffers, and the like. The following illustrates preferred ranges for cleaning compositions for use herein, but is not intended to be limiting thereof.

	<u>Ingredient</u>	<u>% (wt.) Formula Range</u>
25	BPP (Solvent)	0.05-5
	Surfactant	0-2
	Perfume	0.01-1.5
	Water	Balance
	pH range from about 6 to about 8.	
30	Other solvents or co-solvents which can optionally be used herein include various glycol ethers, including materials marketed under trademarks such as Carbitol, methyl Carbitol, butyl Carbitol, propyl Carbitol, and hexyl Cellosolve, and especially methoxy propoxy propanol (MPP), ethoxy propoxy propanol (EPP), propoxy propoxy propanol (PPP), and all isomers and mixtures, respectively, of MPP, EPP, and BPP, as well as butoxy propanol (BP), and the like, and mixtures thereof. If	
35	used, such solvents or co-solvents will typically comprise from about 0.5% to about	

2.5%, by weight, of the aqueous compositions herein. Non-aqueous (less than 50% water) compositions useful herein can comprise the same solvents.

Dispenser - In the preferred mode herein, the dispenser comprises a container for the liquid cleaning composition, said container having a dispensing means which comprises a spout, preferably in the form of a hollow tube, which is connected to said container and is in communication with the interior of the container. In-use, a portion of the liquid composition within the interior of said container flows from the container through said spout, out the distal tip of said spout, and onto the stain which is being treated. The user manipulates the composition by daubing, smearing, pressing, or the like, using the distal tip which impinges on the protective covering material to work the composition into the stain. A circular, rubbing motion is typical. By this means, the composition can be focused on the stained area. As the stain is loosened by the combined use of the aforesaid mechanical manipulation (the force of which is transmitted through the protective material and onto the fabric being treated) and the cleaning composition, the stain residues and the composition are transferred away from the fabric and into the underlying stain receiver. The fabric is then preferably re-positioned so that a fresh area of stain receiver underlies other stained areas, and the process is repeated until the stain removal operation is completed. The fabrics can then be used, as desired, or otherwise laundered or dry-cleaned.

The following Examples illustrate the invention in more detail, but are not intended to be limiting thereof.

EXAMPLE I

A process for removing stain from a localized area on a fabric is conducted by:

- (a) preferably, underlaying the area containing said stain with an absorbent material, e.g., absorbent toweling, or, more preferably, a TBAL ASRA or a FAM-foam absorbent;
- (b) overlaying said area of stain with a sheet of organza fabric in direct contact with the stain as the protective material;
- (c) applying a liquid cleaner (pre-spotter) composition of Example II to said stain from a container having a dispenser spout; and
- (d) rubbing or pressing the distal tip of the spout on the sheet of organza overlaying the stain, thereby driving said cleaning composition into said stain, whereby said stain is transferred into the absorbent material and the fabric being treated is protected from abrasion.

In this mode, the face of the distal tip of said spout can be concave, convex, flat, or the like. A typical dispenser ("dispenser" being the container plus spout for the purposes of this Example) herein has the following dimensions, which are not to be considered limiting thereof. The volume of the container bottle used on the dispenser is typically 2 oz. - 4 oz. (fluid ounces; 59 mls to 118 mls). The larger size container bottle can be high density polyethylene. Low density polyethylene is preferably used for the smaller bottle since it is easier to squeeze. The overall length of the spout is about 0.747 inches (1.89 cm). The spout is of a generally conical shape, with a diameter at its proximal base (where it joins with the container bottle) of about 0.596 inches (1.51 cm) and at its distal of 0.182 inches (4.6 mm). The diameter of the channel within the spout through which the cleaning fluid flows is approximately 0.062 inches (1.57 mm). In this embodiment, the channel runs from the container bottle for a distance of about 0.474 inches (1.2 cm) and then expands slightly as it communicates with the concavity to form the exit orifice at the distal end of the spout.

EXAMPLE II

Examples of preferred, high water content compositions for use in the stain removal operation herein are as follows. The compositions are listed as "nonionic" or "anionic", depending on the type of surfactant used therein.

<u>Ingredient</u>	<u>Nonionic (%)</u>	<u>Anionic (%)</u>
Butoxypropoxypropanol (BPP)	2.00	2.00
NEODOL 23 6.5	0.250	---
NH ₄ Coconut E ₁ S*	---	0.285
Dodecyldimethylamine oxide	---	0.031
MgCl ₂	---	0.018
MgSO ₄	---	0.019
Hydrotrope, perfume, other minors	---	0.101
KATHON preservative	0.0003	0.0003
Water	97.750	97.547

*Ammonium salt of C₁₂-C₁₄ (coconut alkyl) ethoxy (EO-1) sulfate.

EXAMPLE III

A liquid stain cleaning composition is formulated by admixing the following ingredients.

<u>Ingredient</u>	<u>% (wt.)</u>
BPP	4.0
C ₁₂ -C ₁₄ AS, Na salt	0.25

Water and minors*

Balance

*Includes preservatives such as KATHON® at levels of 0.00001%-1%, by weight.

The fabric to be treated is laid flat on an absorbent TBAL stain receiver sheet or any of the other ASRA's or FAM absorbent disclosed herein, and 0.5 ml-4 ml of the composition are dispensed onto the stain either directly or through the porous protective material which is used to cover the stain. The composition is worked into the stain by applying mechanical force to the protective material at the stain site using the tip of the dispenser. Other cleaning devices such as arcuate brushes, solid probes, rubber spatulas, and the like, can be used to provide the mechanical force.

Other useful compositions which can be used in this step are as follows:

<u>Ingredient</u>	<u>Percent (wt.)</u>	<u>(Range; wt.)</u>
BPP	4.0	0.1-4.0%
C ₁₂ -C ₁₄ AS	0.4	0.1 - 0.5%
Nonionic Surfactant (optional)*	0.1	0 - 0.5%
15 Water (distilled or deionized)	Balance	95-99.8%

Target pH = 7.0

*The optional nonionic surfactants in the compositions herein are preferably C₁₂-C₁₄ N-methyl glucamides or ethoxylated C₁₂-C₁₆ alcohols (EO 1-10).

The foregoing illustrates cleaning compositions using an AS surfactant. Improved cleaning performance can be achieved using MgAES and amine oxide surfactants, although possibly with some reduction in phase stability. Thus, aqueous compositions with ca. 2-3% BPP can be stabilized using MgAES surfactants. However, for compositions containing 4%, and higher, BPP, the formulator may wish to include AS surfactant. The amount and blend of surfactants will depend on the degree of temperature-dependent phase stability desired by the formulator. Amine oxide surfactants such as dimethyl dodecyl amine oxide can also be used in the compositions.

While the process and components thereof have been described herein both broadly and in detail, modifications thereof which meet the foregoing considerations fall within the spirit and scope of the present invention. Kits according to the present invention conveniently contain from about 1 to about 6 of the sheet-form ASRA's or sheet-form FAM absorbent, bottled portions (typically about 10 ml to about 100 ml) of the liquid cleaning composition, and 1 to about 10 sheets of the protective covering material. However, larger or smaller quantities of the protective sheets, receivers and/or the cleaning composition can be provided.

WHAT IS CLAIMED IS:

1. In a process for removing stains from a localized area of a fabric with no or minimal visible fabric damage, comprising the steps of applying a cleaning composition to said stain and, concurrently or consecutively therewith, applying mechanical action to said stain by means of a cleaning device, the improvement which comprises covering the stain with a sheet of protective covering material which minimizes abrasion of the fabric caused by the mechanical action of the cleaning device.
2. A process according to Claim 1 wherein the cleaning composition is a liquid.
3. A process according to Claim 2 wherein the liquid cleaning composition comprises water and surfactant.
4. A process according to Claim 2 comprising water, surfactant and organic solvent.
5. A process according to Claim 4 wherein the composition comprises water, butoxy propoxy propanol, MgAES surfactant and amine oxide surfactant.
6. A process according to Claim 1 wherein the cleaning device comprises the dispenser tip of a bottle.
7. A process according to Claim 1 wherein the tip is concave, convex or flat.
8. In a process for removing stain from a localized stained area on a fabric, comprising:
 - (a) placing the stained area of the fabric over and in contact with an absorbent material;
 - (b) applying a liquid cleaning composition to said stain from a container having a dispenser spout; and
 - (c) concurrently or consecutively with step (b), rubbing or pressing said cleaning composition into said stain using the distal tip of said spout, whereby said stain is transferred into the absorbent material, the improvement which

comprises covering the stain with a sheet of protective covering material which minimizes abrasion of the fabric caused by the mechanical action of the spout tip.

5 9. A process according to Claim 8 wherein the tip of said spout is concave.

10 10. A process according to Claim 8 wherein the tip of said spout is convex.

10 11. A process according to Claim 8 wherein the tip of said spout is flat.

15 12. A process according to Claim 8 wherein said cleaning composition comprises water, a solvent and a surfactant.

15 13. A process according to Claim 12 wherein the surfactant comprises a mixture of MgAES surfactant and amine oxide surfactant.

20 14. A process according to Claim 12 wherein the solvent is butoxy propoxy propanol.

15 15. A process according to Claim 8, wherein the absorbent stain receiver is a FAM-foam receiver.

25 16. A process according to Claim 8, wherein the absorbent stain receiver is a ASRA receiver.

17. A process according to Claim 16 wherein the ASRA is a TBAL stain receiver.

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(21) International Application Number: PCT/US98/15003 (22) International Filing Date: 20 July 1998 (20.07.98) (30) Priority Data: 60/053,190 21 July 1997 (21.07.97) US (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): STRANG, Janine, Morgens [US/US]; 3988 Superior Avenue, Deer Park, OH 45236 (US). SIKLOSI, Michael, Peter [US/US]; 7299 Bobby Lane, Cincinnati, OH 45243 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: BR, CA, JP, MX, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: FABRIC STAIN REMOVAL METHOD		
(57) Abstract Disclosed is a process for removing stains from a localized area of a fabric, comprising the steps or applying a cleaning composition to said stain, and concurrently or consecutively therewith, applying mechanical action to said stain by means of a cleaning device. During the treatment, the stain is covered with a protective material which minimizes damage to the fabric due to mechanical action of the cleaning device.		

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled Fabric Stain Removal the specification of which

☐ is attached hereto.

☒ was filed on July 20, 1998 as United States Application No. or
PCT International Application Number PCT/US98/15003
and was amended on (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations §1.56.

I hereby claim foreign priority benefits under Title 35 United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

Priority Claimed

(Number)

(Country)

(Day/Month/Year Filed)

☐ ☐
Yes No

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

60/053,190

July 21, 1997

Application Serial No.

Filing Date

Application Serial No.

Filing Date

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT International application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (If applicable)

As named inventor, I hereby appoint the following registered practitioner(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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